PREPARATION OF Pt/Al_2O_3 FOR PREHEATING SYSTEM ON AUTOTHERMAL REFORMER FOR FUEL CELL

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"I declare that I have read this thesis and in my opinion this thesis is adequate in terms of scope and quality for the purpose awarding a Bachelor's Degree of Chemical Engineering (Gas Technology)."

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Date : 15 May 2008

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
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MAY 2008

I declare that this thesis entitled "*Preparation Of Pt/Al_2o_3 For Preheating System On Autothermal Reformer For Fuel Cell* " is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature:
Name: QUSYAIRI BIN ALI
Date: 06 MAY 2008

To my parents and all of my family for their love.

All the teachers I have had and

to whom I owe so much

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ABSTRACT

Preheating system for autothermal reformers (ATR) is needed to ensure shorter start-up times due to the heat supplied to the catalyst bed by catalytic combustion of the fuel. Nobel metals such as platinum, have been used as catalysts for the catalytic oxidation of hydrogen and show higher activity. However, the platinum catalyst will involve a very high cost because of the platinum price it self. Accordingly, the preparation of platinum catalyst to an alumina support has been investigated in this study. The sample Pt/Al_2O_3 catalyst was prepared with different platinum weight loading which is 1wt% and 3wt% by impregnation process. hexachloroplatinic acid (H_2PtCl_6) and Gama-alumina (γ-Al_2O_3) solutions were used in this preparation. The hydrazine NH_4 added to reduce the chlorine ion from Platinum during preparation. Procedures and condition of impregnation, drying and calcination was discussed. Catalyst characteristic was analysed using Fourier Transform Infra-Red (FTIR) spectroscopy and Scanning Electron Micrograph (SEM). Comparison with literature FTIR data indicated that platinum was dispersed into γ-Al_2O_3. SEM micrograph show that crystallites structure of platinum was formed at γ-Al_2O_3 surface. In addition, both samples were tested through catalytic combustion of hydrogen at fixed air and fuel ratio. The result shows that the 3wt% of Pt/ γ-Al_2O_3 performance is better than 1wt% of Pt/ γ-Al_2O_3 with the highest temperature of 362^{o}C. This temperature is enough to supply the heat to the Autothermal reformer catalyst for it to function efficiently.

ABSTRAK

Sistem pra-pemanasan untuk ATR adalah perlu bagi memastikan masa permulaan lebih pendek dengan membekalkan haba kepada bahagian mangkin melalui pembakaran bermangkin. Logam terpilih seperti platinum, telah digunakan sebagai mangkin untuk pengoksidaan bermangkin kepada metana dan menunjukkan pengaktifan tertinggi. Namun demikian, mangkin platinum akan melibatkan cos yang tinggi disebabkan harga platinum tersebut. Sejajar dengan itu, penyediaan mangkin platinum dengan sokongan alumina telah dicadangkn dalam penyelidikan ini. Sampel mangkin Pt/Al_2O_3 telah disediakan dengan berlainan kandungan berat platinum iaitu 1% dan 3% melalui proses *Impregnasi.* Larutan Gama-alumina (γ-Al_2O_3) dengan heksakloroplatinik asid (H_2PtCl_6) telah digunakan dalam penyediaan ini. Hidrazin NH_4 tambah untuk menurunkn ion klorin daripada platinum semasa penyediaan. Tatacata dan kondisi imprignasi, pengeringan dan *Calsinasi* di bincangkan. Ciri-ciri fizikal mangkin diuji dengan menggunakan Perubahan Fourier Sinar Infra-Mareh (FTIR) spektroskopi dan Imbasan Elektron Mikrograf (SEM). Perbandingan dengan kajian FTIR yang lepas, didapati data taburan platinum keatas γ-Al_2O_3 berlaku. SEM mikrograf menunjukkan pembentukan struktur kristal platinum diatas permukaan γ-Al_2O_3. Tambahan pula, kedua-dua sampel di uji melalui pembakaran bermangkin pada nisbah bahan bakar dan udara yang tetap. Keputusan ujian menunjukkan pencapaian 3wt% of Pt/ γ-Al_2O_3 adalah lebih baik berbanding 1wt% of Pt/ γ-Al_2O_3 dengan suhu maksimun adalah 362 darjah selsius. Suhu ini cukup bagi membekalkan haba kepada mangkin ATR untuk berfungsi dengan berkesan.

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LIST OF ABBREVIATIONS

ATR	–	Autothermal Reformer
CPO	–	Catalytic Partial Oxidation
FTIR	–	Fourier Transform Infrared spectroscopy
HTS	–	High Temperature Shift
PEMFC	–	Proton Exchange Membrane Fuel Cell
SMR	–	Steam Methane Reforming
SEM	–	Scanning Electron Micrograph
TEM	–	Transmission Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of study

The automobile industry is under a great deal of pressure to produce and market low emission vehicles. Beginning in 2003, 10 percent of vehicles offered for sale in California will be required to be zero-emission vehicles. Other states are also moving toward this objective. (Fuel Cell 2000)

Fuel cells show great promise as a replacement to internal combustion engines in automobiles due to their high efficiency, low or zero emissions, and quiet, continuous operation. The Proton Exchange Membrane fuel cell (PEMFC) has additional advantages because of its low operating temperature, high power density, and advanced stage of technical development. The PEMFC uses hydrogen, which is not easily transported or stored.

For these reasons, and in order to take advantage of the existing fuel infrastructure, the PEMFC needs to be integrated with a fuel processor that can use methane that can be conveniently distributed. Figure 1.1 illustrates the chemical unit operations necessary to process fuel and how the system is integrated with a PEMFC.

In the production of hydrogen, it is well known in the art to treat hydrocarbon material with a catalyst at high temperatures in the presence of steam. Autothermal reforming is an approach that combines catalytic partial oxidation and steam reforming. Partial oxidation employs substoichiometric combustion to achieve the

temperature to reform the fuel. Fuel, oxidant (oxygen or air, for example), and steam are reacted to form primarily hydrogen, CO_2 and CO.

An advantage of autothermal reforming technology is that the exothermic combustion reactions are used to drive the endothermic reforming reaction. Autothermal reforming typically employ noble metal catalyst beds operating at temperature of about 870^{o}C to about 1300^{o}C. In comparison to steam reformers, and advantage of autothermal reformers is that at these high operating temperatures, sulfur in the fuel, which is present primarily as H_2S, does not significantly poison the catalyst and permit downstream sulfur remover. (Richerd, 2002)

A further advantage of autothermal reformers is that start-up times also tend to be shorter due to the heat supplied to the catalyst bed by catalytic combustion of the fuel.

1.2 Problem statement

Preheating System for autothermal reformers needed to ensure start-up times also tend to be shorter due to the heat supplied to the catalyst bed by catalytic combustion of the fuel.

Catalyst in the preheating system is used to perform catalytic combustion. One of factor that influences the combustion performance is catalyst activity. Nobel metal such as Pt, have been used as catalysts for the catalytic oxidation of methane and show higher activity.

However, the platinum catalyst will involve a very high cost because of the platinum price it self. So, the other alternative is to prepare platinum catalyst are usually dispersed on a support in order to increase cost efficiency. The catalysts are being supported by a highly porous and thermally stable material (such as alumina) onto platinum which the active species are being dispersed to form Platinum Alumina (Pt/Al_2O_3) catalyst. The main purpose of a support is to achieve an optimal

dispersion of the catalytically active component(s) and to stabilize it against sintering.

1.3 Objective

The main objectives of this research are:

i) To study the method of preparation Pt weight loading over alumina support catalyst.

ii) To find the optimum temperature by catalytic combustion of hydrogen with fixed air fuel ratio.

1.4 Scope of research

In order to fulfill the objectives, the scopes of the study are:

i) Preparation of Pt/Al_2O_3 catalyst with different weight loading which is 1wt% and 3wt% from hexachloroplatinic acid (H_2PtCl_6) by using impregnation method.

ii) Analysed catalyst characteristic in order to know the dispersed of platinum and the structure of support.

iii) Tested the catalyst through catalytic combustion at fixed air and fuel ratio to get the temperature profile.

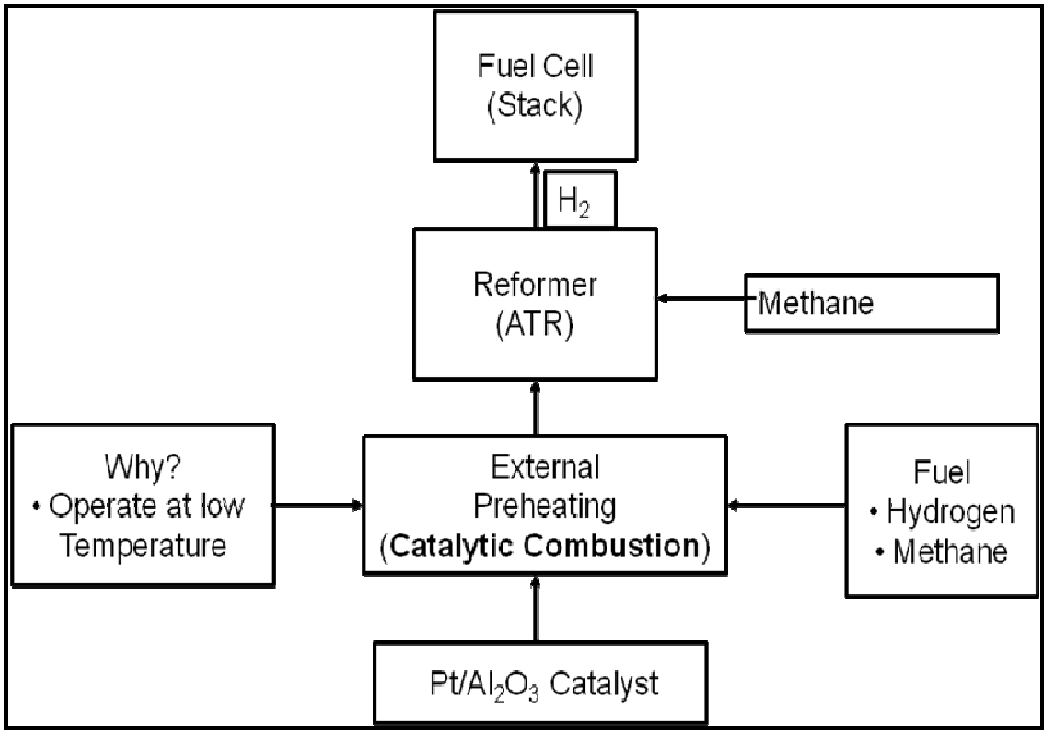

Figure 1.1: Fuel Processor/Fuel Cell System

CHAPTER 2

LITERATURE REVIEW

2.1 Preparation of Platinum Catalyst

Olsbye, et al. (1996) proposed "Impregnation of platinum metal was performed using an aqueous solution of H_2PtC1_6 (Hexahydrat zur Synthese, Merck). The impregnation method basically followed [1], with the following procedure. The impregnation was performed in a shaking waterbath at 20°C under an inert atmosphere (N_2). In order to prevent light promoted dissociation of the complex [2], the experiments were performed in complete dark, with the exception of red light illumination during sampling and work-up. The H_2PtC1_6 solution (0.005M, 150 ml) was added to a three-neck flask. The pH of the solution was initially 2.2. It was adjusted by adding either HCl (1M) or NaOH (1M). The relationship between NaOH addition and pH in the different starting solutions is shown in Table 1. Then the alumina (3 g) was added and the mixture was left with shaking for a given contact time. The pH of the solution was monitored by a pH-meter (Oakton RS232). It should be noted that measurement of pH in the solution caused diffusion of KCl from the electrode into the solution, affecting the Cl-analyses considerably. Samples of the solution (2 ml) were withdrawn using a pipette, filtered (S and S Filter paper circles, 5893 ashless Blue ribbon) and stored in closed sample holders. After completing the impregnation, the solution was filtered from the alumina, and the solid was dried (90°C, 2 h). The catalyst was wet calcined (air saturated with water at 65°C) at 570°C for 120 min., and then further calcined in dry air at 570°C for 60 min."

Freni, et al. (1999) proposed “The washcoating procedure proceeds through the impregnation of the frame structure by an aqueous slurry of $-Al_2O_3$ of powders190 m^2/g, 2 3 porositys80%-25 mm. and HCl. After impregnation, monoliths are slowly dried, at 100°C, and calcinated at 550°C, under a flow of air. This process can be repeated two or more times in order to enhance the amount of deposited alumina. The most delicate step in the process is the dispersion of the metal salts from which the catalyst will be obtained.”

Ma L., et al. (1995) proposed “A Pt/αA1_20_3 catalyst was made in the laboratory. γ-A1_20_3 was calcined at 1273K (4 h) to produce a product shown to be mainly &A1203 by X-ray diffraction. The surface area was 130 m 2 g-1. This material was crushed and sieved to 250-500 μm. A calculated amount of chloroplatinic acid was dissolved in water to give a solution of volume ca. 2 × the pore volume of the support. The solid was mixed with the liquid and gently stirred at room temperature for 3 h. The slurry was then dried at 330-343 and 393K overnight. Calcination at 773 K (4 h) was followed by reduction at the same temperature (H_2:4 h). Once the catalyst had been reduced, no further reduction was necessary, even after exposure to air. The catalyst was found to have a BET surface area of 128 m 2 g-I and a metal surface area, measured by CO adsorption and assuming 1" 1 stoichiometry, of 0.35 m 2 g^{-1}.”

Yem, et al. (2007) proposed “Pt/γ-Alumina catalysts were synthesized by impregnation of different supports. The required amount of 8 wt% liquid H_2PtCl_6 dissolved in 50 mL of water was directly impregnated onto the four types of supports. As a rule, the metal loading on the support corresponded to 5 wt%. The temperature was increased to 70°C and the mixture was stirred vigorously in a closed beaker for 3 h. Then, after adsorption equilibrium had been reached, the excess water was removed using a rotary evaporator. The catalyst was then dried overnight in air at 120°C, followed by calcination in a 100 mL/min air flow for 2 h. Reduction was accomplished using a 50 mL/min H2 flow for 2 h at 400°C. The hydrogenation of a mixture of 1-hexene and *n*-heptane at a 1-hexene/*n*-heptane molar ratio of 1:8 was carried out using a fixed bed reactor under continuous flow and atmospheric pressure. The sample amounts used were 0.375 g. The reaction temperature

investigated was 30°C. The products were analyzed online by a gas chromatograph equipped with a flame ionization detector."

Shelimov, et al. (1999) proposed "Al_2O_3 (15 g) was added to 250 ml of 0.1 M HCl at pH 1.4, and the mixture was stirred for 4 h until pH 4.0 was reached. The excess HCl was then removed, and 200 ml of 0.1M HCl was added followed by stirring for 3 h until pH 1.7 was attained, decanting, filtering the powder, and drying it at 90°C overnight. A stock ($6.6x10^2$ M) H_2Pt_Cl6 solution at pH 1.15 was used for alumina impregnation; it was prepared by diluting a 8 wt% aqueous solution of H_2PtCl_6 (Aldrich) with water. The pH values were measured using a Tacussel PHN-850 digital pH meter. No change in pH was found to occur for the aged stock solution. A less acidic H_2PtCl_6 solution at pH 2.83 also used for alumina impregnation was prepared by adding 1 or 0.1 M NaOH to the stock H_2PtCl_6 solution. This solution was aged for at least 2 days before alumina impregnation. H_2PtCl_6/α-Al_2O_3 samples were prepared by adding the H_2PtCl_6 solution to alumina upon continuous stirring at 20°C. The volume of the impregnating solution was typically twice greater than the alumina pore volume. After impregnation, the samples were first dried in a dessicator over P_2O_5 under vacuum and then in air at 90 and/or 150°C and finally calcined at a higher temperature. The Pt content in the impregnated alumina samples was 1.5 wt%."

Corro, et al. (2005) proposed "The support used was α-Al_2O_3 Merck with a grain size of 0.063–0.200 mm (70–230 mesh ASTM). Before use, the support was calcined for 6 h at 600°C in air. Pt catalyst supported on alumina was prepared by impregnation using acidic aqueous solutions (0.1 M HCl) of H_2PtCl_6 X $6H_2O$ (Merck, min. 98% purity). After impregnation, the catalyst was dried at 120 _C overnight, and then calcined in flowing air for 6 h at 500°C. Finally, the catalyst was reduced in pure hydrogen flow for 8 h at 500°C. A reference alumina support was prepared in the same way using only diluted hydrochloric acid. A sample of the reduced catalyst was then sulfated. Sulfation was performed on the sample heating to 500°C in flowing air (100 cm3 min_1). The feed was then changed at 500°C for a nitrogen flow containing 50 ppm SO2, 5%O2 (100 cm3 min_1) for 10 h. The samples were then cooled to 25°C."

Catalysis Letters 70 (2000) 109–116 proposed "Pt/Al_2O_3 was prepared by the wet impregnation technique. For this purpose, a solution of $H_2PtCl_6 \cdot 6H_2O$ in water (0.01 g Pt / ml) and Al_2O_3 (000–3AQ, AKZO, The Netherlands) were used. The Al_2O_3 was obtained by extruding the gel. The pellets were crushed and sieved to particles with diameters between 0.3 and 0.6 mm. The grains were calcined for 15 h at 1125 K (heating rate 3 K / min) in flowing air (30 ml / min) and subsequently impregnated with Pt (0.5 wt%). The catalysts were dried at 365 K for 2 h in a rotating evaporator followed by drying overnight at 395 K in static air. The impregnated grains were calcined for 15 h at 925 K (heating rate 3 K / min) in flowing air (30 ml/min). The Pt content of the catalysts was determined by atomic absorption spectroscopy."

Applied Catalysis A: General 255 (2003) 83–92 proposed "The γ-Al_2O_3 support (Harshaw, Al 3996) was calcined in flowing air at 550^oC for 2 h. The ZrO_2 support was prepared by calcination of zirconium hydroxide (MEL Chemicals) using the same conditions. The 10% ZrO_2/Al_2O_3 was obtained by impregnation of alumina with a nitric acid solution of zirconium hydroxide, as described elsewhere [13]. The supports were impregnated with an aqueous solution of chloroplatinic acid (H_2PtCl_6, Aldrich) by incipient wetness technique. The catalysts were subsequently dried overnight at 120^oC and calcined in air at 550^oC for 2 h. The platinum content was around 1 wt. %"

Catalysis Letters Vol. 91, Nos. 1–2, (2003) Proposed "Al_2O_3, ZrO_2 and CeO_2 supports were prepared by calcination of γ-alumina Engelhard Corporation Catalyst), zirconium hydroxide (MEL Chemicals) and cerium ammonium nitrate (Aldrich) at 550^0C for 2 h under flowing air. The platinum catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of chloroplatinic acid (H_2PtCl_6, Aldrich), followed by drying at 120^oC for 16 h and calcinations in air at 550^oC for 2 h. All samples contained about 1 wt% of platinum, which was determined by atomic absorption spectrometry. The prepared catalysts are referred to as PtAl for Pt/Al_2O_3, PtZr for Pt/ZrO_2 and PtCe for Pt/CeO_2."

Applied Catalysis B: Environmental 75 (2007) 59–70 proposed “Preparation of the catalyst-precursor: the support was a commercial γ-Al2O3 (Alfa Aesar, 99.97%; grain size = 3 mm) dispersed in water (1 l of distilled water per 4 g of g-Al_2O_3) and then impregnated with an aqueous solution (1 M) of $(NH_3)4Cl_2.H_2O$ (M = Pd, Pt; Aldrich, 99.99+%), the final pH is adjusted at 10.6 by adding ammonia solution (NH_4OH 25%, Fisher Scientific) dropwise; once the solvent has been evaporated at a reduced pressure in a rotavapor at 323 K, the solid is allowed to dry overnight at 383 K (the weight percentages of Pt-Pd are listed in Table 1); the catalysts are denoted as Pt(x)-Pd(y)/g-Al_2O_3, where x and y are the weight percentages of platinum and palladium, respectively.”

2.2 Preparation of Noble Metal Catalyst

Nohaira, et al. (2005) proposed “The various supports were ground and then sieved to retain particles with sizes between 0.10 and 0.04 mm. The monometallic Pd based catalysts were prepared either via cationic exchange of the support (SiO_2) by Pd $(NH_3)4(NO_3)2$ in basic medium (pH = 11) or via simple impregnation (Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$) using the same Pd precursor. The monometallic catalysts were dried overnight at 120 ◦C, then calcined in flowing air at 300°C for 4 h, and finally reduced under hydrogen flow at 400°C for 4 h. The Pd/TiO_2 catalyst was reduced at 300°C instead of 400°C in order to avoid the SMSI effect. Bimetallic Pd–Pb catalysts were prepared by the surface redox reaction between hydrogen activated on palladium particles and the lead precursor ($Pb(CH_3COO)_2$) dissolved in methanol (“catalytic reduction” method [26]). This preparation method of bimetallic catalysts is well known to induce a strong interaction between the two metals whatever the prepared bimetallic system [27–29]. A known amount of the prereduced palladium catalyst was introduced into a reactor under nitrogen and was activated at 300°C for 1 h under hydrogen. Then the solution of the lead precursor in methanol, previously degassed under nitrogen flow, was introduced onto the catalyst at room temperature. After a 1 h reaction time under hydrogen bubbling, the solution was filtered out and the catalyst was dried overnight at 100°C. Finally, the bimetallic catalysts were reduced under hydrogen flow at 300°C for 2 h (2 ◦C/min heating rate).

Using the same approach, a blank Pd catalyst over SiO_2, named "Pd1 treated in CH_3OH/H_2" further in the text, was also prepared in a methanol solution without addition of the lead precursor."

Tichit, et al. (2007) proposed "The initial Mg/Al/NO_3 LDH was prepared by coprecipitation at constant pH (_10) of aMg and Al nitrates solution (Mg/ Al: 0.75/0.25) with a solution of NaOH (1.0 M). The addition rate of the alkaline solution and the pH were controlled by using a pH-STAT Titrino (Metrohm) apparatus. The suspension was stirred overnight at 353 K for 17 h, and then the solid was separated by centrifugation, rinsed thoroughly with distilled water (Na < 100 ppm) and dried overnight at 353 K. The Mg(Al)O mixed oxide support was then obtained by activation of Mg/Al/NO3 LDH in air-flow at 773 K for 3 h (heating rate: 3 Kmin_1). Mg(Al)O was impregnated with Pd acetylacetonate (Pd(acac)2, Aldrich) in water-free toluene solution for 12 h. After solvent evaporation the solid was dried at 353 K in vacuum, calcined for 3 h in air flow at 773 K, then reduced with H2/N2 (10/90, v/v) at 523 K for 5 h (heating rate: 1 K min_1)."

Kurzina, et al. (2006) said "For the study on the influence of the support nature on the catalytic performances of the catalysts, the catalysts were prepared by impregnation of the different supports (a-$Si3N_4$, b- $Si3N_4$, SiN-am and SiN-annl) with adequate amounts of Pd(II)- bis-acetylacetonate [$Pd(C_5H_7O_2)_2$] dissolved in toluene. For the study on the influence of the solvent used in the preparation method on the catalytic performances of the catalysts, these were prepared by impregnation of a-Si3N4 with adequate amounts of Pd(II)-acetate [$Pd(CH_3CO_2)_2$] dissolved either in toluene or in water. In both cases, we used an excess of solvent. After impregnation, evaporation of the solvent and drying, the catalysts precursors were decomposed under argon flow at 500^oC for 2 h. They were then calcined during 2 h at 350^oC under oxygen flow and further reduced under hydrogen flow at 500^oC (in both cases the heating rate was 1 K min^{-1}). The content of Pd is always 0.5% in weight."

Ji-Jun, et al. (2007) proposed "Pd-B/γ-Al2O3 amorphous alloy catalyst was prepared by the following procedures. γ-Al2O3 powders (Tianjin Chemical Engineering Design Institute, 100–120 mesh) calcined at 550^oC for 2 h were

impregnated with diluted $PdCl_2$ (Xian Kaili Chemical Engineering Company) solution. The initial amount of Pd was defined as 0.4 wt.% for all the experiments. After dried at 120°C for 2 h, the catalysts were pre-calcined at defined temperature for another 2 h. Then they were reduced by adding KBH4 solution (0.2 M) under gentle stirring in an ice water bath for about 30 min until no obvious bubbles were observed. The resulting black solid powders were washed thoroughly with oxygen-free distilled water until no Cl− ions were detected in the solution and subsequently with pure alcohol. Thermal annealing was carried out in N_2 atmosphere at defined temperature for 2 h. For X-ray diffractive (XRD) characterization, MCM-41 (Tianda Beiyang Company) was used as the support to avoid the diffraction peaks of Pd being overlapped by those of support. For the purpose of comparison, traditional 0.4 wt. % Pd/γ-Al_2O_3 catalyst was prepared by routine impregnation followed with H_2 reduction at 300°C for 2 h."

Shetian, et al. (2003) proposed "The Pd/ZnO catalysts were prepared by either impregnation (IMP series) of a ZnO support (Sakai Co.) with $Pd(NO_3)_2$ aqueous solution (10% $Pd(NO_3)_2$ in 10% HNO3 from Aldrich) or by co-precipitation (CP series) of $Zn(NO_3)_2$ + $Pd(NO_3)_2$ with NaOH + Na_2CO_3 aqueous solutions at constant pH and room temperature. $Zn(NO_3)_2{\cdot}6H_2O$, NaOH, and Na_2CO_3 of analytical grade were from wako chemicals. Pd weight loading for IMP samples was 1–10%, and the nominal Pd loading of CP samples was 1–15%. Thecatalysts were named according to their preparation method and nominal Pd loading. For example, the sample prepared by IMP method with 3.5% Pd was designated as IMP3.5, and the sample prepared by CP method with 15% Pd was designated as CP15, and so on. All the samples were finally calcined at 450 ◦C for 2 h and crushed to 0.15–0.25mm for activity test."

Benkhaled, et al. (2006) Proposed "The preparation method used an aqueous solution of palladium nitrate (Herau¨ s) and a defined quantity of NaNO2 (Aldrich 99.99%), corresponding to a molar ratio NO2/ Pd = 4. Incipient wetness impregnations were realized in a rotating beaker. After drying at 393 K, the catalyst was calcined under airflow at 473 K during 2 h and finally reduced under hydrogen flow. In order to remove residual Na, a washing step with water was performed. FTIR and thermogravimetric analysis of Pd[NO2] catalysts were performed on

samples before the washing step. These catalysts are here referred as Pd[NO2]nw (as ‘‘not washed’’ samples). The palladium loading was varied from 0.1 to 0.6 wt.% and two types of alumina support were used: a d-Al2O3 (specific surface area SBET = 130 m2/g and porous volume Vp = 1.04 cc/g), and a gc-Al2O3 (SBET = 200 m2/g, Vp = 0.6 cm3/g). These catalysts are labeled here as 130 or 200Pdx ($1 < x < 5$). In order to make a comparison, two others catalysts have been prepared starting from bis-acetylacetonate (Strem 99%) in organic medium. The desired amount of $Pd(C_5H_7O_2)_2$ is dissolved in 300 ml of toluene and added to 20 g of α-Al_2O_3 (referred as 130Pd[acac]) or γ- Al_2O_3 (200Pd[acac]) for 72 h at room temperature under stirring. The mixture is then filtered and washed 3 times with 100 ml of distilled water. After drying at 393 K during 12 h, the catalyst is finally calcined in an air flow at 623 K during 2 h.”

Wang, et al. (2007) Proposed “The Rh-based catalysts were prepared by impregnation followed by drying at 110ºC for 12 h and calcination at 500ºC for 2 h in air. All Rh contents were 1% (Rh/Ce molar ratio = 1.2). Prior to the pulse reactions, the catalysts were reduced in H_2 (20 ml/min) at 500ºC for 0.5 h and then heated to 700ºC in Ar. A CH_4 pulse (300.58 μl) was passed over the catalyst and the effluents were analyzed by a gas chromatograph equipped with a TCD. In situ CO-FTIR and Py-FTIR experiments were carried out on a Bruker Equinox 55 Fourier spectrometer.”

James, et al. (2006) proposed”γ -Al_2O_3 (UOP LaRoche VGL-15) was used for preparing 20 wt% CeO_2–Al_2O_3 (Ce–Al) by wet impregnation of $Ce(NO_3)_2$ followed by calcination at 550°C. For the Rh loading, $Rh(NO_3)_3$ was wet-impregnated onto the prepared Ce–Al support. Our preliminary work indicated that the Rh catalyst derived from $Rh(NO_3)_3$ was better than that derived from RhCl3 in terms of better metal dispersion and improved catalyst activity for reforming. The impregnated catalyst was then dried at 100°C overnight, followed by calcination at 550°C, for a nominal Rh loading of 2 wt% for all catalysts studied. For the Rh–Ni bimetallic catalysts, unless described otherwise, the Ni and Rh were co-loaded via wet co-impregnation using a solution of the respective metal nitrates, then dried overnight at 100°C, followed by calcination at 550°C. Several control catalysts were

prepared with a different support (the γ -Al_2O_3 without CeO_2) using the same impregnation procedure."

Duprez, et al. (2003) proposed "The support used was a high-surface-area ceria (HSA) provided by Rhodia Rare Earths (BET area, 60 m2 g−1; grain size, about 50 μm; no internal porosity; main impurity, La ≈ 2000 ppm). In order to avoid possible sintering of the oxide during the pretreatment of the catalyst, the support was pretreated at high temperature before impregnation: reduction under H2 at 900°C followed by calcination under air at 450°C. The BET surface was then reduced to 23 m^2 g^{-1}. The catalyst was prepared by impregnation of the pretreated support (5 g) with an aqueous solution of rhodium III nitrate $Rh(NO_3)_3$ from Fluka. The slurry was gently shaken at room temperature on an oscillating table for 16 h. The supernatant solution was evaporated to dryness on a sand bath maintained at 60°C. The catalyst batch was subsequently dried at 120°C and calcined in an air flow at 450°C for 4 h before storage. After impregnation, the metal content was 3.7 wt% in rhodium."

2.3 Summary of Catalyst Preparation

Table 2.2 show the summary on catalyst preparation of platinum alumina. There have ten articles on past research explain the condition during preparing step using impregnation method. Table 2.3 then show the preparation condition of noble metal catalyst using a various method.

Table 2.2: Preparation of Platinum Alumina by Impregnation Method

Article	List of Chem.	stir	pH measure	dry	calcine	Reduction
Unni Olsbye 1996	H_2PtCl_6 (Merck). HCl (1M) or NaOH (1M). alumina	20°C under an inert atmosphere	pH of the solution was initially 2.2. It was adjusted by adding either HCl (1M) or NaOH (1M)	90°C, 2 h	(air saturated with water at 65°C) at 570°C for 120 min., and then further in dry air at 570°C for 60 min.	
S. Eyni 1999	H_2PtCl_6 γ-Al_2O_3 HCl			at T=100°C	at T=550°C under a flow of air	
D.L. Trimm 1995	γ-Al_2O_3 chloroplatinic acid (CLA)	at room temperature for 3 h		330-343 and 393K overnight.	773 K (4 h) was followed by	reduction at the same temperature (H2:4 h)
Jai Neung Kim 2007	liquid H_2PtCl_6 four types of supports	70°C for 3 h		overnight in air at 120°C	in a 100 mL/min air flow for 2 h.	accomplished using a 50 mL/min H2 flow for 2 h at 400°C.
Boris Shelimov 1999	Al_2O_3 0.1 M HCl 0.1 M NaOH H_2PtCl_6 solution	=20°C	mixture was stirred for 4 h until pH 4.0 was reached	desiccators over P_2O_5 under vacuum and then in air at 90 and/or 150°C	at a higher temperature	

Article	List of Chem.	stir	pH measure	dry	calcine	Reduction
Grisel Corro 2005	γ-Al2O3 (Merck) 0.1 M HCl $H_2PtCl_6*6H_2O$ nitrogen		by impregnation using acidic aqueous solutions	at 120°C overnight	flowing air for 6 h at 500°C	hydrogen flow for 8 h at 500°C (sulfation) nitrogen flow containing 50 ppm SO2, 5%O2 (100 cm3 min_1) for 10 h.
Catalysis Letters 70 (2000)	$H_2PtCl_6*6H_2O$ (0.01 g Pt / ml) Al_2O_3			365 K for 2 h in a rotating evaporator And drying overnight at 395 K	15 h at 925 K (heating rate 3 K / min) in flowing air (30 ml/min).	
General 255 (2003)	γ-Al_2O_3 support (Harshaw, Al2O3, 1996) nitric acid (H_2PtCl_6 , Aldrich)			overnight at 120 °C	550 °C for 2 h in air	
Catalysis Letters Vol. 91, 2003	(H_2PtCl_6 , Aldrich), Al_2O_3, ZrO_2 and CeO_2			120 °C for 16 h	550 °C for 2 h in air	
Applied Catalysis Environmental 75 (2007)	γ-Al_2O_3 $(NH_3)_4Cl_2*H_2O$ NH_4OH(1 M)	rotavapor at 323 K	pH is adjusted at 10.6 by adding ammonia solution (NH_4OH 25%, Fisher Scientific) dropwise	overnight at 383 K		

Table 2.3: Preparation of Noble metal Catalyst by Various Method

Article	List of chem.	Stir	pH measure	Dry	Calcine	Reduction
Bendsoud Nohaira 2005	$Pd(NH_3)_4(NO_3)_2$ Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$			overnight at 120 ˚C	in flowing air at 300 ˚C for 4 h	under hydrogen flow at 400 ˚C for 4 h
Bendsoud Nohaira 2005 Didier Tichit 2007	Mg and Al nitrates solution NaOH (1.0 M). Pdacetylacetonate ($Pd(acac)_2$,Aldrich)	overnight at 353 K for 17 h	rinsed thoroughly with distilled water (Na < 100 ppm)	overnight at 353 K	In air-flow at 773 K for 3 h (heating rate: 3 Kmin_1).	with H2/N2 (10/90, v/v) at 523 K for 5 h (heating rate: 1 K min_1).
F.J. Cadete Santos Aires 2006	a-$Si3N_4$, b- $Si3N_4$, SiN-am and SiN-annl $Pd(C5H7O_2)_2$			under argon flow at 500^0C for 2 h	2 h at 350^0C under oxygen flow	under hydrogen flow at 500^0C (in both cases the heating rate was 1 K min_1)
Ji-Jun Zou 2007	γ-Al_2O_3 powders $PdCl_2$			dried at 120 ˚C for 2 h	550 ˚C for 2 h	adding KBH4 solution(0.2M)under gentle stirring in an ice water bath for about 30 min
M. Benkhaled 2006)	palladium nitrate $NaNO_2$	rotating beaker		drying at 393K	under airflow at 473 K during 2 h	Under hydrogen flow.